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ALLYLIC RADICALS WITH CAPTODATIVE SUBSTITUTION : EASY HOMOLYSIS OF 1,5-HEXADIENES.[1]

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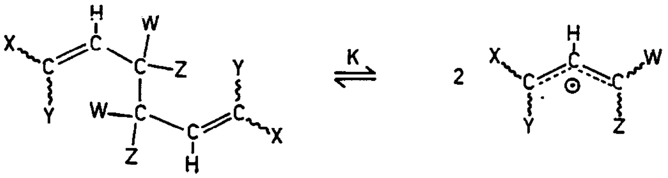
Summary : Dissociation of the new 1,3,4,6-captodative substituted 1,5-hexadienes **1** to 1,3-bis-captodative allylic radicals **4** has been observed around room temperature. Dissociation enthalpies ΔH vary from 8 to 25 Kcal/mol. In contrast the dimer **3a** of the 1,3-bis-dicapto allylic tetraester radical dissociates to **6a** only around 140°C (ΔH = 38.1 Kcal/mol). The replacement of one of the olefinic ester groups on carbons 1 and 6 in **3a** by a donor substituent (without influencing the crowding around the central C-C bond), such as in **2a** and **b** lowers ΔH from 38.1 to 24.0 and 28.2 Kcal/mol respectively. These results demonstrate the synergy for radical stabilisation by captodative substitution.

The radical stabilisation by captodative (**cd**) substitution[2] has been investigated with several methods[1,2,3]. We report now on the C-C bond homolysis of **cd** and dicapto(**cc**)-substituted 1,5-hexadienes **1-3** which dissociate to allylic radicals **4-6** with varying ease depending on their substitution pattern.



1,2,3 4,5,6

1,4 : X,W = **d** Y,Z = **c**
2,5 : X = **d** Y,W,Z = **c**
3,6 : X,Y,Z,W = **c**

c = captor (electron acceptor) substituent **d** = dative (electron donor) substituent

Dissociation is observed at temperatures lower than 50°C for all the dimers **1a-f** (Table 1) of the 1,3-bis-**cd** radicals. When pairing for **cd** substitution the nitrile group with SR or NR_2, arise dimers with the highest degree of dissociation, as judged by the intensity and the low appearence temperature (-50°C) of the ESR signal. In contrast to these bis-**cd** substituted radicals, the 1,3-bis-**cc** radical **6a** (**c** = COOMe) deriving from **3a** is only observable at temperatures higher than 140°C. If one of the olefinic ester groups in **6a** is replaced by a donor substituent (**5a,b**), the temperature of the ESR signal appearance is lowered to ∿ 70-80°C.

ESR spectra have been analysed and confirm the structures of the radicals **4 to 6**. These spectroscopic results will be published elsewhere as well as the syntheses of the new 1,5-hexadienes **1-3** obtained by the oxidation of the allylic anions[4,5]. All hexadienes have been isolated except **1a**, which has been formed in situ and is recognised by the reversible variation with temperature of the ESR signal intensity of its radical **4a**.

In order to evaluate quantitatively the influence of **cd**-substitution on the C-C bond dissociation of these 1,5-hexadienes the enthalpies of dissociation (ΔH_{diss}) were determined. The ΔH_{diss} was calculated[6] from the variation of ESR signal intensity with temperature. Results are listed in Table 1 together with the hyperfine coupling constants of the β-protons, characterising the torsion angle in allylic radicals [7].

	X	Y	W	Z	a^{β} (Gauss)	ΔH_{DISS} (Kcal/mol)	ΔS_{DISS} (cal/mol.K)	ΔG_{DISS}[(a)] (at 300°K) (Kcal/mol)	$K^{(a)}$ (at 300°K)
1a $\rightleftharpoons$ 4a	NMe$_2$	CN	NMe$_2$	CN (b) (c)		8.08 ± 0.25			
b	St-Bu	CN	St-Bu	CN (c) (g)	3.67	13.50 ± 0.26	16.7 ± 4.0	8.49	6.20×10^{-7}
c	SEt	CN	SEt	CN (c) (g)		13.40 ± 0.25			
d	OMe	CN	OMe	CN (c) (h)	3.50	24.47 ± 0.44	27.6 ± 2.9	16.19	1.46×10^{-12}
e	OEt	CN	OEt	CN (c) (h)	3.55	24.70 ± 0.33			
f	SMe	COOMe	SMe	COOMe (e) (h)		23.11 ± 0.46			
2a $\rightleftharpoons$ 5a	SMe	COOMe	COOMe	COOMe (f) (i)	5.42	23.98 ± 0.42			
b	OMe	COOMe	COOMe	COOMe (d) (i)	4.17	28.22 ± 0.15	30.7 ± 2.0	19.01	1.24×10^{-14}
3a $\rightleftharpoons$ 6a	COOMe	COOMe	COOMe	COOMe (d)	5.53	38.11 ± 0.11	40.5 ± 1.8	25.96	1.05×10^{-19}
7 $\rightleftharpoons$ 8	COOMe	COOMe	S-CH$_2$-CH$_2$-S (e)		2.5	23.2 ± 0.2			

(a) At 300°K

(b) Radical 4a generated by heating of 1,3-N,N-tetramethyldiamino-1,3-dicyano propene with t-butyl peroxyde to 120°C, ΔH determined between 20-90°C.

(c) Chlorobenzene solution

(d) o-Dichlorobenzene solution

(e) Diphenylether solution

f) o-Xylene solution

g) Meso/D,L mixture of E,E-1,5-hexadienes

h) Mixture of meso/D,L and Z/E 1,5-hexadienes

i) Pure Z,Z-1,5-hexadiene.

TABLE 1. Thermodynamic data for the homolysis of 1,5-hexadienes **1,2,3** leading to allylic radicals **4,5,6**.

When equilibrium constants (K) have been determined with precision ΔS and ΔG are also given, and the corresponding plots of the experimental values are shown in Figure 1.

These thermodynamic data give only enthalpy - or free energy - differences between the hexadiene ground state and the corresponding allylic radicals. Before deriving from these results a relative order of radical stabilising power of substituent couples it would first be necessary to account for steric effects both in the allylic radicals and in their dimers. Secondly the stabilisation (or destabilisation) in each dimer should be known. So far only estimations are possible. Nevertheless three hexadienes **2a**, **2b** and **3a** permit a clear comparison of substituent effects on radical stabilisation because the steric influence on the carbon-carbon bond to be homolysed is constant with always four esters as substituents.

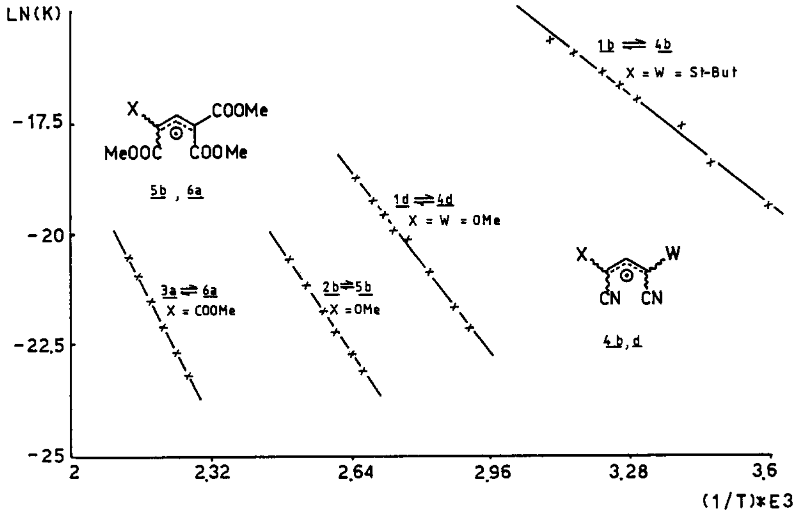
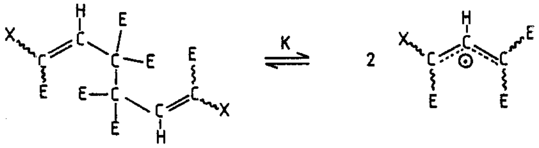


Fig. 1. Correlation of equilibrium constants with temperature.



E = $COOCH_3$	**3a** X = E		**6a**
	2a = SCH_3		**5a**
	2b = OCH_3		**5b**

For the comparison of **6a** to **5b** one has to take into account the following considerations: For the radicals, the increased ESR-coupling constant reveals for **6a** (a^{β} = 5.53 G) a slight deviation from coplanarity whereas **5b** (a^{β}= 4.17G) appears nearly planar[7]. The resulting loss of conjugation in **6a** might be compensated by the higher radical stabilising power of an ester than that of a methoxy group[8]. For the dimers, generally donor substituents such as the OR group in **2b** stabilise double bonds better than the electron withdrawing ester group in **3a** [9,10]. Therefore a lower ground state- and higher dissociation-enthalpy could be predicted for **2b**, while if additivity of individual radical stabilisation energies would apply the tetracapto-allylic radical **6a** should be at least as stabilised as **5b**. Consequently **3a** should have at most the dissociation energy of **2b**. In contrast to these expectations **2b** exhibits ΔΔG=7 Kcal/mol less free energy of dissociation than **3a**. These results can only be explained by synergism on radical stabilisation by **cd** and antagonism for dicapto(**cc**)-substitution.

The bis-**cd** substituted allylic radical dimers **1a-f** exhibit the same relative order of dissociation enthalpy values as observed in other independant studies[2,3] on radical stabilisation with coresponding substituent couples. Differences in steric effects do not decisively determine the relative order of dissociation enthalpies because only four of the eight radical stabilising substituents influence sterically the bond dissociation. Thus varying S-t-butyl (**1b**) for S-ethyl (**1c**) substitution practically makes no difference on ΔH_{diss}.

The only example of an allylic **cd** system with 1,1-bis donor and 3,3-bis captor substitution **7**$\rightleftharpoons$**8** shows the same dissociation enthalpy as the 1,3-bis **cd** analog **1f**.

For the four compounds, for which equilibrium constants have been determined, important variations are observed on entropy change (ΔS = 17 to 40 cal/Kmol, see Table 1) with an entropy/enthalpy compensation. We consider that these variations are due to solvent/solute interaction[11]. As a consequence of this entropy/enthalpy compensation for the measurements in solution the free energy change seems to give the best indication for the relative radical stabilisation power of substituents. In our study these ΔG data lead to the same conclusion: Synergisme for captodative substitution.

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5) In contrast to the easy oxidative coupling to hexadienes **1a-f, 2a-b** and **3a** the octacyano substituted diene **3b** (X,Y,W,Z = CN) has not yet been obtained, probably because of the high stabilisation of the tetracyano-allyl anion.
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8) This comparison can be made on the basis of a Relative Radical Stabilisation (RRS_x)scale: RRS_{OMe} = 4.5, RRS_{COOMe} = 7.9 and RRS_{SMe} = 10.7.See in "Substituent Effects in Radical Chemistry", H.G. Viehe, Z. Janousek, R. Merényi Editors, NATO ASI Series, D. Reidel Pub. Co., Dordrecht, 1986 p. 313.
9) In the Chemistry of allylic dimers we have two indications for this difference in the double bond stabilisation : a) The kinetic product of the anion oxydation to obtain **2a** and **b** is the 1,4-**cc**-3,6-**cd** dimer; equilibration leads to the 1,6-**cd**-3,4-**cc** hexadienes **2a** and **b** ; ΔH_{diss} were measured on these last type of dimers. b) Correspondingly by thermal elimination $PhS(O)C(COOMe)_2-CH_2-CH(OMe)(COOMe)$ gives $(MeOOC)_2CH-CH=C(OMe)(COOMe)$, the thermodynamic product, see ref.4).
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11) This phenomenon will be discussed elsewhere. Similar radical forming reactions from highly substituted substrates show an analogous isokinetic or isoequilibrium relationship. Cf. ref.8 p.310.

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